

Recent advances in mercury removal technology at the National Energy Technology Laboratory[☆]

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Abstract

The in-house research effort on mercury studies at the National Energy Technology Laboratory is an integrated, multi-task approach, including experimentation at both the laboratory-scale and the pilot-scale, as well as a numerical modeling effort to aid in interpretation of pilot-scale results. In the laboratory-scale work, novel sorbents and techniques for the removal of mercury from flue gas are being investigated using a small packed-bed reactor. The reactor system is used to screen novel sorbents for their capability to remove mercury from gas streams. The capacities of these novel sorbents are determined as a function of gas composition and temperature and are compared to results with commercially available activated carbons. In the pilot-scale work, an existing pilot unit has been characterized with respect to the distribution and fate of hazardous air pollutants in flue gas, with an emphasis on mercury. The pilot unit is a 500-lb/h (227-kg/h) pulverized coal-fired (PCFC) combustion system that includes a furnace, air preheater, spray dryer, ductwork and a pulse-jet fabric filter. The investigations with this unit have entailed evaluation of various activated carbons and novel sorbents, as well as comparisons of various sampling techniques for the determination of total and speciated forms of mercury. The impact of various parameters (temperature, sorbent-to-mercury ratio, baghouse pressure drop) on the removal of mercury has been investigated. Additionally, a slipstream allows for the investigation of sorbent injection in a fly ash-free flue gas over a wide range of operating conditions, including residence time. A summary of the results for mercury measurement and control from the 500-lb/h (227-kg/h) PCFC combustion system will be presented, as well as the evaluation of methods for measurement of in-

[☆] Reference in this paper to any specific commercial product, process or service is to facilitate understanding and does not necessarily imply its endorsement by the United States Department of Energy.

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duct removals using the slipstream. Finally, a discussion of the numerical modeling effort will be given.

1. Introduction

The scrutiny of mercury (Hg) emissions from coal-fired utilities that began with the Clean Air Act Amendments of 1990 (CAAA) has resulted in a determination by the U.S. EPA that such emissions should be regulated. Furthermore, the current administration has proposed a Clear Skies Initiative that includes a provision that will cap mercury emissions from electric utilities. In the past decade, a number of techniques for control of mercury emissions from power plants have been evaluated at various scales. One technique that has received a great deal of attention by the EPA, utilities and technology developers is dry sorbent injection upstream of an existing particulate control device.

The in-house mercury research effort at NETL is implemented at both the laboratory-scale and pilot-scale. The laboratory-scale research objectives are to develop cost-effective sorbents through evaluation in a packed-bed reactor and to investigate novel mercury removal techniques, such as a photochemical method for mercury control. Results from the laboratory work support the pilot work. The pilot-scale work has been directed to evaluate methods for mercury measurement and to assess the technical performance of mercury control technologies by developing engineering databases. The mercury measurement methods that have been evaluated at the pilot-scale include the wet chemical methods (e.g., the Ontario-Hydro ASTM Method), the Frontier Geosciences solid sorbent speciation method and a semi-continuous emissions monitor manufactured by P.S. Analytical. Recent testing has included the use of a novel probe device developed by Apogee Scientific, for measuring vapor-phase mercury in the presence of fly ash and/or an active mercury sorbent to determine in-duct removals.

The mercury control technology being evaluated at the pilot scale is dry, sorbent injection upstream of a pulse-jet baghouse. Initial work focussed on characterizing the 500-lb/h (227-kg/h) combustion system in terms of the distribution and fate of mercury, while combusting eastern bituminous coals. Afterwards, a series of tests were conducted on this unit to initiate operation of a sorbent injection system and obtain a data base on mercury removal with the injection of a commercially available activated carbon (Darco® FGD). A low-sulfur ($\sim 1\%$), bituminous coal from the Evergreen mine was used for these tests. This type of coal (near compliance coal) is burned by utilities that do not have flue gas desulfurization systems. For these utilities, sorbent injection may be the most cost-effective option for control of mercury, depending upon the nature of the emissions regulations that might be enacted. Having established the performance of Darco® FGD in the 500-lb/h (227-kg/h) system, the effects of operating conditions (e.g., baghouse pressure drop and humidification) on mercury removal have been explored, and the performance of novel sorbents have been compared to the performance of the benchmark Darco® FGD. In order to provide insight into the data obtained from the pilot-scale

system, a numerical model has been developed that incorporates sorbent parameters, such as the isotherm coefficients, as well as operating conditions, such as the variation in filter cake thickness with time and bag cleaning frequency.

2. Laboratory-scale investigations

A schematic of the packed-bed reactor is shown in Fig. 1. The carrier gas for the elemental mercury can be argon, as shown in Fig. 1, nitrogen, air or a simulated flue gas. The simulated flue gas contains carbon dioxide (16%), oxygen (5%), sulfur dioxide (2000 ppm), nitric oxide (500 ppm) and nitrogen (balance). When the carrier gas is argon, an on-line atomic fluorescence spectrophotometer monitors the elemental mercury concentration in the inlet and outlet streams of the reactor. Breakthrough curves and sorbent capacity are determined from these measurements. For more complex carrier gases, only sorbent capacity is determined off-line by analyzing the spent sorbent with a cold vapor atomic absorption spectrophotometer after a prescribed time.

The operating temperature range for the packed-bed reactor is from ambient temperature to about 400 °F (204 °C). During a test, the reactor temperature and the concentration of elemental mercury in the inlet gas are held constant. Details on the design and operation of the experimental apparatus have been provided previously [1]. Additionally, the same reactor system can be modified to investigate novel techniques for

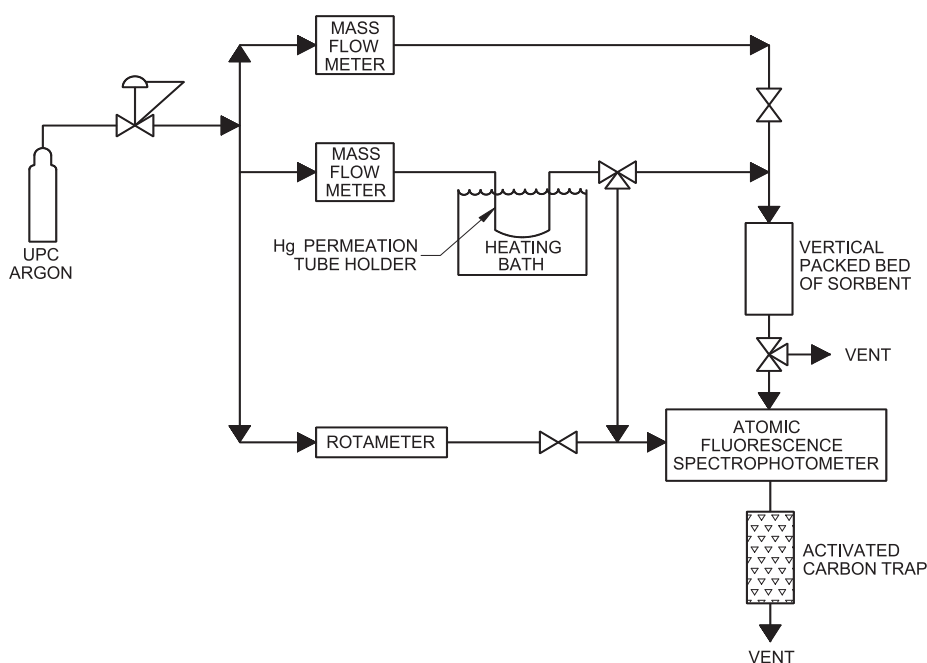


Fig. 1. Schematic of sorbent screening unit.

Table 1
Activated carbon capacities measured in packed-bed reactor

Sorbent	Capacity (mg/g)	Temp. (°F)
FluePac	0.89	280
Darco FGD	1.60	280
Insul	1.96	280
Insul	0.19	400
S-AC-1 ^a	1.55	280
S-AC-2 ^a	1.39	280

^a S-AC-1 and S-AC-2 are sulfur promoted activated carbons.

mercury control. The photochemical reactor work, described elsewhere [2], is an example of this.

Typical results of screening tests with activated carbons are shown in Table 1. The measured capacities for the activated carbons were near 1–2 mg mercury/g sorbent and ranged from 0.19 mg/g for Insul at 400 °F (204 °C) to 1.96 for Insul at 280 °F (138 °C). These results indicate that unpromoted carbons display good capacity and sulfur promotion does not significantly increase capacity. Further, it appears that physical adsorption is favored by low temperature. In addition to activated carbons, the types of sorbents that have been examined include metal oxides, metals sulfides and fly ash-derived sorbents [1]. In addition, the packed-bed is also being used in the evaluation of a novel sorbent from a process currently being developed in-house.

3. Pilot-scale equipment and operations

3.1. 500-lb/h (227-kg/h) PCFC pilot unit description

The 500-lb/h (227-kg/h) PCFC system consists of a pulverized coal wall-fired furnace equipped with a water cooled convection section, a recuperative air heater, spray dryer, baghouse and associated ancillary equipment (fin-fan coolers, surge tanks, coal hoppers, blowers, pumps, etc.). The 500-lb/h (227-kg/h) combustor is an indirect-fired unit. Coal is first pulverized off-line in the Williams roller mill and then transported through a series of hoppers before it is fed by an Acrison weight-loss differential feeder to the combustor. The wall-fired, dry bottom type combustor is capable of firing both coal and/or natural gas. The combustor's four wall-fired burners are equipped with secondary air registers that can be adjusted to improve combustion. On-line temperature readings, flow measurements and four separate banks of continuous gas analyzers (O₂, NO_x, CO, SO₂ and CO₂) characterize the overall system operating performance.

A wide range of flue gas temperatures can be obtained at the duct test section, baghouse and stack. The options for altering the flue gas temperature include indirect cooling by adjusting system operating conditions and/or direct cooling by humidification. Also, sorbent can be injected at numerous locations along the duct test section, allowing for a wide range of sorbent in-duct residence times relative to the baghouse and gas sampling locations. A schematic diagram of the 500-lb/h (227-kg/h) PCFC system is shown in Fig. 2.

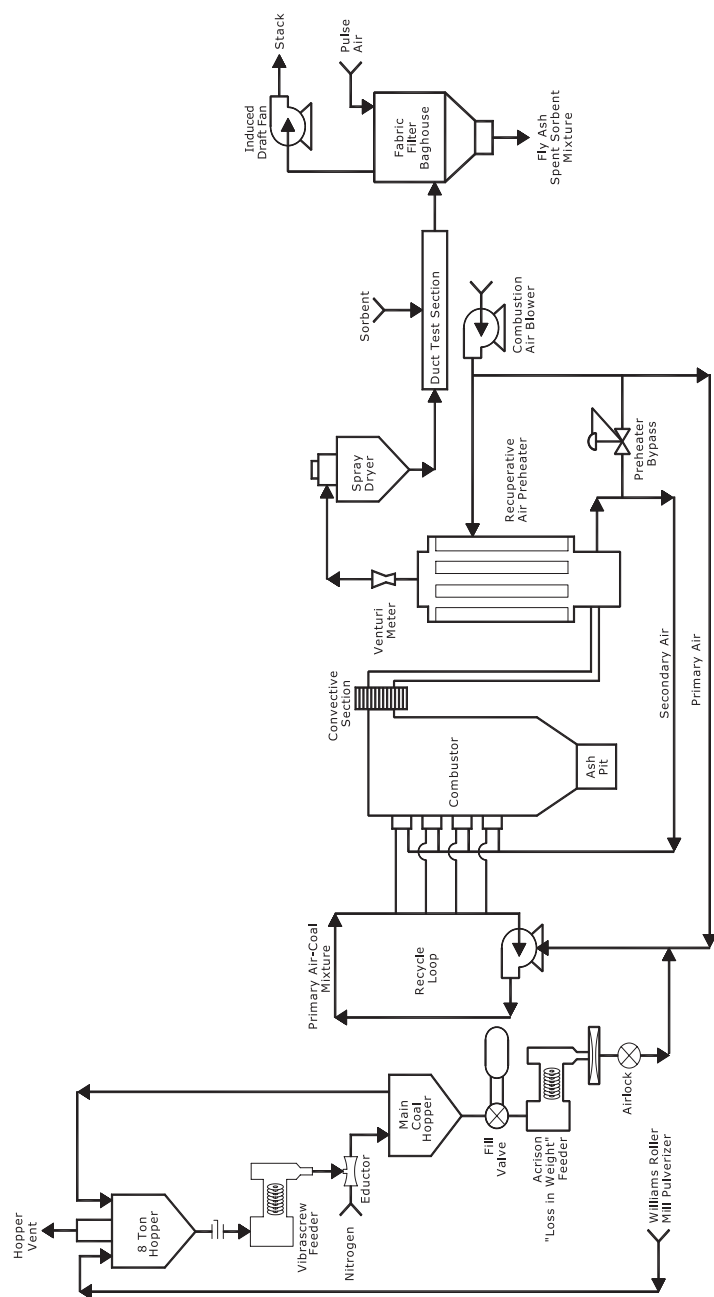


Fig. 2. Schematic of the NETL 500 lb/h coal combustion test facility.

A more detailed description of the combustion, humidification and sorbent injection has been given previously [3,4].

3.2. CERF unit description

A state-of-the-art pilot-scale Combustion and Environmental Research Facility (CERF), with a nominal rating of 500,000 Btu/h (146 kW), is NETL's principal facility to assess the performance of typical pulverized/suspension-fired systems. The CERF consists of a vertical down-fired combustor, convective section, pulse-jet baghouse, secondary air preheater and associated ancillary equipment (coal storage bins, ID fan, etc.). The CERF is well-instrumented (flue gas analyzers, thermocouples, flow meters, etc.) with a personal computer-based data acquisition and process control system. The CERF uses a single-register burner whose design was based on the moveable-block swirl generator concepts developed by International Flame Research Foundation. The CERF burner allows for an accurate adjustment of secondary air swirl number based on the offset position of a series of precisely machined triangular blocks formed from a solid plate that rests upon a fixed plate with triangular blocks of the same thickness. The CERF is designed for precise combustion control while allowing independent control of its baghouse temperature, and this is desirable when investigating the effects of combustion efficiency on Hg removals.

3.3. Description of slipstream duct

In order to eliminate the confounding effects of varying unburned carbon levels in fly ash, a slipstream has been constructed which provides a fly ash-free, coal-derived flue gas for tests of sorbent injection. The slipstream has provisions for temperature control of the duct surface and multiple locations for mercury spiking and sorbent injection. This slipstream duct was designed for a flow of about 200 actual cubic feet per minute ($0.094 \text{ m}^3/\text{s}$), or about one-tenth that of the full flow from the 500-lb/h (227-kg/h) unit. The duct consists of 3-in. (0.076 m), stainless steel, Schedule 10 pipe and is installed from the exit of the 500-lb/h (227-kg/h) combustion unit baghouse to the inlet of the baghouse of the CERF unit. This arrangement provides a near particulate-free flue gas and a temperature-controlled duct with a residence time up to 4 seconds.

3.4. Operating conditions

For consistency, a single low-sulfur bituminous coal from the Evergreen mine was fired in both the 500-lb/h (227-kg/h) PCFC and CERF for all the testing described here. The average analysis of the low-sulfur bituminous coal used in all the testing on the CERF and 500-lb/h (227-kg/h) PCFC is shown in Table 2. Throughout the sorbent injection testing, the 500-lb/h (227-kg/h) PCFC was intentionally operated to achieve high combustion efficiency with low unburned carbon levels in the fly ash. Both the 500-lb/h (227-kg/h) PCFC and CERF combustors typically operate in the range of 3–4% O_2 at the furnace exit, with a primary air/total air greater than 20%. The purpose of maintaining low unburned carbon levels in fly ash is to minimize the effects of unburned carbon acting as a mercury sorbent. For the 500-lb/h (227-kg/h) PCFC system, it was found previously that

Table 2
Average coal analysis (Determined from 61 daily composites)

	Average, as received	Standard deviation
Heating value, Btu/lb	12,989	120
Moisture, %	1.16	0.26
Mercury, ppm	0.09	0.02
Chlorine, ppm	1247	94
Ultimate analysis, wt. %		
Carbon	73.42	0.89
Hydrogen	5.01	0.21
Oxygen	6.69	0.77
Nitrogen	1.41	0.03
Sulfur	0.99	0.08
Ash	12.49	0.63

minimal effects from the fly ash could be expected at unburned carbon levels near 1% [1]. The major operating variables that have been investigated for their impact on mercury removal have included sorbent injection rate (sorbent/Hg mass ratio), baghouse temperature and the sorbent type.

3.5. Mercury measurements

A sampling team composed of trained in-house NETL researchers conducted all flue gas measurements for mercury. Most of the mercury removals and material balances were calculated from wet chemical flue gas measurements using either EPA Method 101A [5] for total mercury or the ASTM Method [6], also known as the Ontario-Hydro (O-H) method, for total and speciated mercury. These two wet-chemical methods have been supplemented with the solid sorbent method developed by Frontier Geosciences [7], and a semi-continuous emissions monitor (SCEM) was developed by P.S. Analytical [8]. The solid sorbent method and the on-line SCEM have not only been shown to give good agreement with the standard, wet-chemical methods [3], but are also less cumbersome, time-consuming and labor-intensive.

4. Pilot-scale results

For the testing on the 500-lb/h (227-kg/h) unit, the resulting speciation in the ductwork upstream of the baghouse has been very consistent, with the oxidized fraction of the vapor-phase mercury ranging from 75% to 87%, based on the Ontario-Hydro measurements. This is similar to the speciation obtained at full-scale utilities burning similar types of coal. The total mercury material balances around the baghouse and overall system have generally been good. For the numerous sorbent injection tests conducted to date, the balance around the baghouse has averaged 101% while overall system balance has averaged 85% [9]. This suggests that there is excellent consistency for the flue gas and baghouse ash measurements, while there is room for improvement in the overall system (coal/bottom ash/flue gas/baghouse ash) measurements.

4.1. Sorbent injection

A substantial database on sorbent injection for mercury removal has been developed for the 500-lb/h (227-kg/h) PCFC unit through testing at various injection rates and baghouse temperature conditions. The majority of tests were run with Norit Darco® FGD-activated carbon. The Norit Darco® FGD was chosen for most of the tests because it has become a benchmark sorbent for comparing mercury removal results with other sorbents. In this testing, the overall (duct and baghouse) removals ranged from negligible to over 90% at sorbent-to-mercury ratios ranging from 0 to 15,400 and at baghouse temperatures from 250 (121) to 300 °F (149°). These results are displayed graphically in Fig. 3. From the data in Fig. 3, several general conclusions can be made. At a particular baghouse temperature, a trend exists where removals increase with increasing sorbent-to-mercury ratio. Also, near a constant injection ratio, the mercury removal efficiency increases with decreasing baghouse temperature.

4.2. Effects of baghouse operating conditions

There is a continuing investigation into the influence of baghouse operating conditions (such as baghouse pressure drop and cleaning frequency) on mercury removal. The influence of an increasing baghouse pressure drop was initially noticed with the semi-continuous emissions monitor and subsequently verified with a standard manual sampling method. The initial test results, shown in Fig. 3, indicate that increasing baghouse pressure drop from 5 to 8 in. of water (1.2–2.0 kPa) results in an increased mercury removal at low sorbent injection rates. This increase in pressure drop results from an increase in filter cake

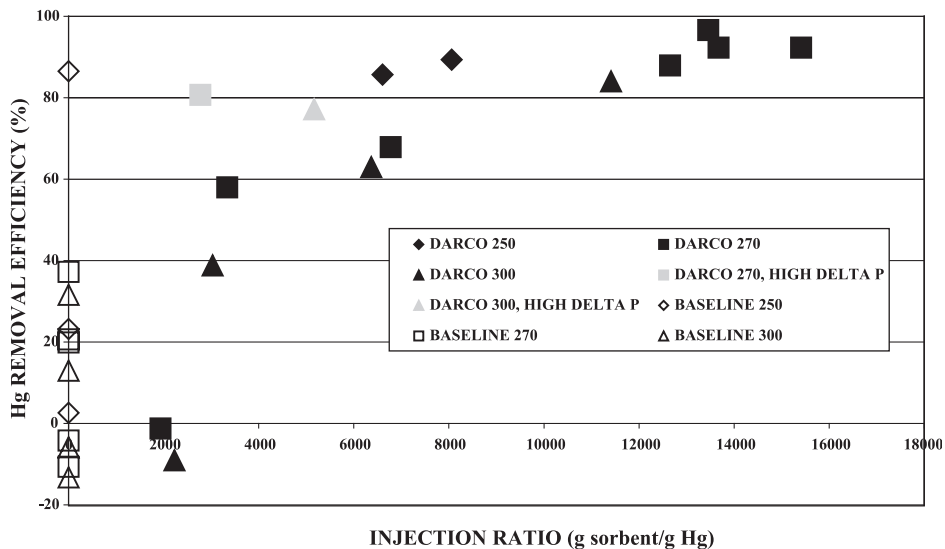


Fig. 3. Mercury removal vs. sorbent injection rate.

thickness at constant system operating conditions. The investigation into the influence (and limits) of baghouse operating conditions on mercury removals is ongoing and is discussed further below in the discussion on the development of the numerical model.

4.3. Effect of unburned carbon in fly ash

The baseline data (i.e., removals with no sorbent injection) situated on the y-axis of Fig. 3 indicate a wide range of removals under the baseline conditions. A highly variable baseline removal could obscure interpretation of the effect of sorbent injection on removals, at least at moderate (<50%) removals. Some of the high removals reported for baseline tests could be due to transient effects (i.e., the baghouse removals had not reached a steady state condition). However, at least some of the variation is probably due to adsorption of mercury by unburned carbon in the fly ash. It was shown previously [4] that negligible removals can be expected burning Evergreen coal in this unit if the unburned carbon level is below 1%. The mercury removals, as a function of baghouse fly ash loss-on-ignition (LOI), shown in Fig. 4 (solid circles), for the baseline operating conditions indicate that very low mercury removals are obtained at low LOI. However, for higher levels, there is the possibility that fly ash carbon could affect mercury removals in the baghouse.

In an attempt to determine the influence of fly ash carbon on mercury removal, a series of tests was conducted on the CERF, and the results are shown in Fig. 4 (open circles). Initially, the baseline CERF combustion conditions were established and Hg concentrations and baghouse removals quantified using wet chemical methods along with the P.S.

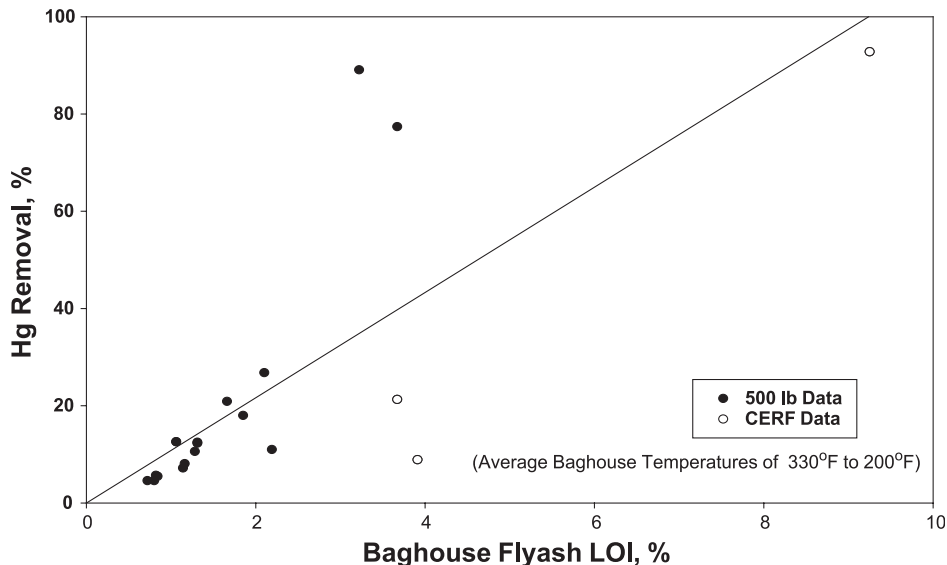


Fig. 4. Effect of baghouse fly ash LOI on mercury removal.

Analytical mercury analyzer. Once the Hg removal was quantified for the initial combustor operation, the combustor swirl setting and excess air were altered in an attempt to decrease combustor efficiency and maximize fly ash carbon. Approximately 33 h (118,800 s) of continuous analyzer data along with results from Method 101A clearly shows that fly ash with significant LOI (carbon) can result in Hg removals of greater than 90% [9]. This information along with previous test data will be supplemented with additional testing in an effort to determine more clearly the effect of fly ash carbon and baghouse temperatures on Hg removals.

4.4. Evaluation of novel sorbents

In addition to commercially available activated carbons, a number of novel sorbents have been tested in the 500-lb/h (227-kg/h) PCFC system. A summary of the results obtained injecting these various sorbents is provided in Table 3. The first novel sorbent tested was a treated zeolite developed by PSI. This sorbent gave a removal of about 60% at a sorbent-to-mercury ratio of about 10,000-to-1, which is slightly lower than Darco® FGD at similar conditions. Two fly ash-derived sorbents were developed in-house. One sorbent was a high carbon fraction derived from fly ash that was at an operating utility. The second sorbent was the same high-carbon fraction from the same fly ash, but activated to increase the surface area. Negligible mercury removal was detected for either sorbent, whereas the Norit Darco® sorbent would remove about 80% of the mercury at similar conditions. A sulfur-promoted, activated, fly ash-derived sorbent was also tested and no measurable removal with the novel sorbent was observed. Another novel sorbent, manufactured by Nucon International and obtained from Dr. Radisav Vidic of the University of Pittsburgh, was tested under similar conditions. This sorbent showed over 70% removal, which is slightly lower than the Darco® FGD, but may be competitive on a cost basis. The last novel sorbent tested was a granulated alumina. Although, this material showed promise in the laboratory-scale tests, there was negligible removal at the pilot-scale.

Table 3
Novel sorbents tested in pilot unit

Sorbent type	Sorbent description	Temp _{BH} (°F)	Injection ratio ^a	Hg _{inlet} (µg/dscm) ^b	Hg removal (%)
PSI sorbent	Treated Zeolite	270	10,400	7.1	63
Fly ash-derived	Carbon from fly ash	261	12,800	6.9	29
Fly ash-derived	Carbon from fly ash-activated	262	7900	9.4	1.3
Fly ash-derived	Carbon from fly ash-activated and sulfur-promoted	270	9400	7.1	– 3.3
Nucon	Sulfur-promoted, activated carbon	270	10,100	7.4	77.5
Alumina	Granulated alumina	270	18,900	6.9	~ 0

^a Injection ratio units are grams of sorbent per gram of mercury.

^b Mercury concentration at the baghouse inlet in micrograms per dry, standard cubic meter, corrected to 3% oxygen.

4.5. Development of a novel process for mercury removal

The observed effects of high carbon sorbents during tests on both the CERF and 500-lb/h (227-kg/h) unit has led to the identification and development of a process (dubbed the “Thief Process”) that may be applicable to a broad range of pulverized coal-fired combustion systems. The process is one where the semi-combusted solid products from coal-firing at high temperatures (in or near the flame) are extracted from the combustor, cooled, transported and then injected into the flue gas downstream of the air preheater. This thermally activated solid reacts with mercury within the flue gas and thus removes it. The spent solid can then be removed from the flue gas by the particulate collection device downstream of the ductwork or by a particulate collection device dedicated solely to the sorbent. A more detailed discussion of the development of this process has been provided previously [10].

Prior to testing at the pilot-scale, samples of the Thief sorbent were evaluated in the lab-scale packed-bed reactor. The results of these tests showed that the Thief sorbent had mercury sorption capacities of 1.4–2.2 mg/g at 280 °F (138 °C), which is similar to that found for Darco® FGD-activated carbon. Tests were then conducted on the 500-lb/h (227-kg/h) unit using the proposed technique for mercury removal. Sample (sorbent) was extracted from the combustion chamber and then injected into the ductwork before the baghouse to remove mercury. A water-cooled probe was inserted into the 500-lb/h (227-kg/h) combustion furnace to collect the sorbent, while the low-sulfur, bituminous Evergreen coal was combusted. The samples were then combined, homogenized into a single batch, and then used as sorbent in subsequent testing with the 500-lb/h (227-kg/h) combustion system. The results of measured removals across the baghouse are shown in Fig. 5, as well as removals obtained with Darco® FGD sorbent at similar conditions. Removals as high as 76% were obtained when injecting the Thief sorbent upstream of the baghouse. Although it is apparent that the removals observed with the Thief sorbent are lower for a given sorbent-to-mercury ratio, the novel process has not been optimized yet and has other advantages which could make it competitive with the commercial sorbent.

4.6. Slipstream tests

Although the pilot unit has been found to give similar mercury removals across the baghouse as seen in full-scale testing of injection of Darco® FGD sorbent in a baghouse configuration, the pilot-scale results can not be directly compared to sorbent injection for mercury capture at full-scale utilities with an electrostatic precipitator (ESP). In an ESP configuration, most of the mercury capture by sorbent is believed to occur within the duct upstream of the ESP; whereas in a baghouse configuration, most of the mercury capture is believed to occur in the filter cake on the bags. In order to expand the applicability of the pilot-scale testing, a method for measurement of in-duct removals is required. The measurement of in-duct removals requires an accurate measurement of the vapor-phase concentration of mercury within a duct in the presence of an active mercury sorbent. The standard reference methods are inadequate for such measurements since the vapor-phase mercury can adsorb on the solids collected on the heated filter during sampling. Therefore, a method for separating the solids entrained in the flue gas without affecting the mercury

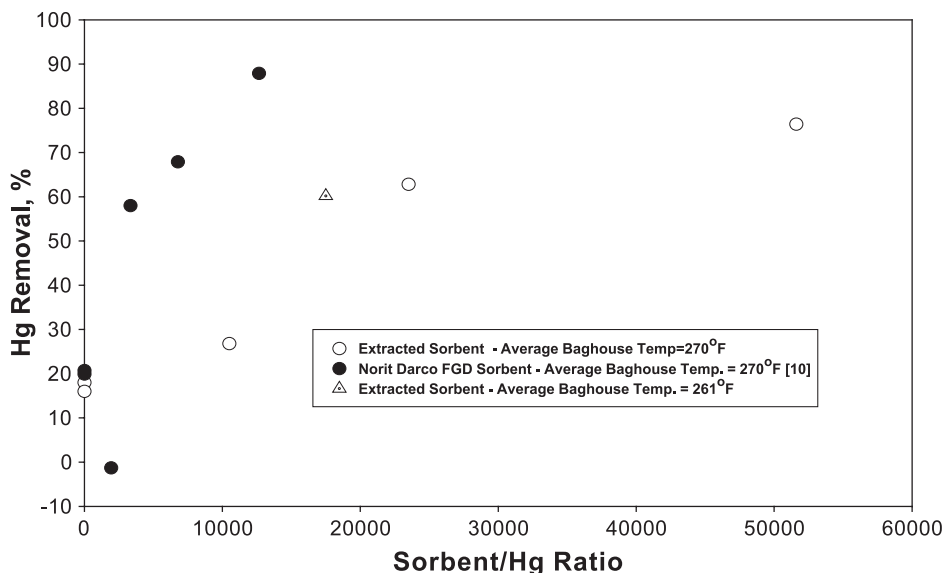


Fig. 5. Comparison of the effectiveness of Darco® FGD and Thief sorbents.

concentration or speciation in the vapor-phase is needed. A series of tests were conducted to evaluate available methods for achieving such a separation, and thus measure in-duct mercury removals.

Initially, it was believed that separation of injected Darco® FGD sorbent from the flue gas would not be especially difficult. The mass mean diameter of the sorbent, as reported by the manufacturer, is 15 μm . In addition, particle sizing by Coulter Counter showed that there was a negligible fraction below 10 μm . Therefore, the first tests in the slipstream duct were conducted using a standard, EPA Method 5-type, glass cyclone, which has a cutpoint of about 10 μm . It immediately became apparent that this method would not be adequate, since almost 50% of the sorbent passed through the cyclone and deposited on the filter.

The next method that was evaluated involved a PM_{2.5} sampling head. This sampling device has a cutpoint of 2.5 μm and is intended for use downstream of a particulate collection device (i.e., low particulate concentration). The separation efficiency of this device ($\sim 70\%$) was better than the cyclone, but still inadequate for making in-duct mercury measurements.

This poor efficiency of the cyclone and PM_{2.5} head was somewhat unexpected given the particle sizing information provided by the manufacturer and the results of the Coulter Counter measurements. However, the separation efficiency of inertial devices is dependent on aerodynamic diameter, rather than physical size. Therefore, testing with an Andersen impactor was conducted. These results showed that a significant fraction ($\sim 40\%$) of the injected sorbent had an aerodynamic diameter below one micron. Furthermore, scanning electron micrographs of the activated carbon also showed a significant number of submicron particles. In-duct measurements of mercury would therefore require a device capable of achieving high efficiency on submicron particles.

After a review of on-going research in methods of solids separation from flue gas, two novel devices under development were identified for evaluation. The first novel method was a virtual impactor, developed under a DOE contract by MSP. This device had shown promise in preliminary bench-scale testing [11]. Although the device was better than the other methods used, there was still a large amount of particulate in the sample gas after the device. Modifications to the installation and operation of the device were made in an effort to improve separation efficiency, but these also proved inadequate.

The second novel device to be considered was developed by Apogee Scientific [12] and had shown promising results in various DOE-funded projects. The device—called the Quicksilver Inertial Separation (QSIG) probe—was obtained and a series of tests were conducted. Initial tests were positive and showed that negligible particulate matter passed through the device and remained in the sample flue gas. Therefore, further tests were conducted to measure in-duct mercury removals using the QSIG probe.

Preliminary measurements of in-duct removals using the QSIG probe in the slipstream duct have been promising. For these tests, the flue gas was generated by the combustion of a low-sulfur, bituminous coal in the 500-lb/h (227-kg/h) combustion unit. The temperature of the slipstream duct was held at 300 °F (149 °C). The residence time of the sorbent in the duct was about 1.3 s. During the tests, the mercury concentration was varied by spiking the slipstream flue gas with elemental mercury. This was done since a secondary objective was to determine whether there was any dependence of in-duct removal on mercury concentration. The sorbent injection rate was also varied to give a range of sorbent-to-mercury ratios.

Measurements for total (i.e., vapor-phase plus solid-phase) mercury were made using standard reference methods (either EPA Method 101A or the Ontario-Hydro Method). As stated earlier, these standard reference methods do not give accurate vapor-solid distribution or mercury speciation in the presence of an active mercury sorbent; however, the total mercury measured should be accurate. The QSIG probe was located just downstream (~5 ft (1.5 m), or less than one-tenth of a second residence time) of the sampling location for the standard reference methods. Mercury concentrations were monitored at the QSIG probe using a semi-continuous emissions monitor (SCEM). After steady-state conditions were established based on the readings from the SCEM, a mercury sample was obtained from the QSIG using a solid sorbent method developed by Frontier Geosciences, referred to as the Frontier Mercury Solid Sorbent (FMSS) method. An example of the use of the SCEM to establish steady-state conditions and typical mercury measurements obtained with the SCEM, FMSS and Ontario-Hydro method are shown in Fig. 6. The results shown in this figure indicate that the SCEM coupled with the QSIG responds rapidly to changes in mercury concentration resulting from either mercury spiking or sorbent injection. Note that after completion of the triplicate sampling with Method 101A and the FMSS method at steady-state conditions, the sorbent injection rate was varied, then shut off, and then the mercury spiking was stopped. The mercury concentrations as measured by the SCEM responded as expected. Also, the average total and elemental mercury concentration determined with the SCEM is in good agreement with that obtained with the FMSS method. An interesting note is that, although elemental mercury was spiked into the flue gas, both the SCEM and FMSS method found that almost all the mercury was in the oxidized form at the outlet of the slipstream duct. The conversion of the elemental mercury

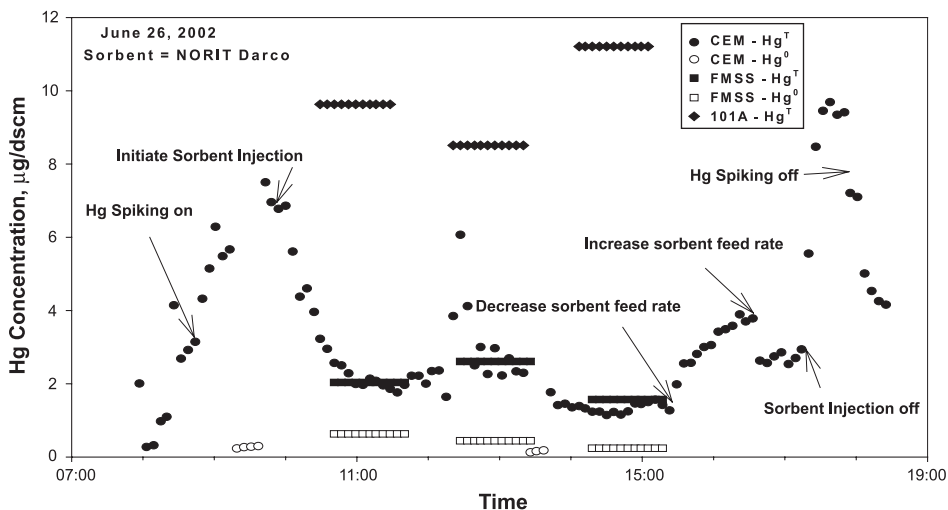


Fig. 6. Slipstream testing using the QGIS probe.

either occurred in the slipstream duct, in the QGIS probe, or in both. Additional investigation is needed to determine the cause. Finally, the difference between the total mercury concentration obtained with the standard reference method (Method 101A in the case of Fig. 6) and the SCEM or FMSS method represents the difference between total mercury and vapor-phase mercury, which is attributed to in-duct removal of mercury by the sorbent.

4.7. Development of mathematical model

As stated earlier, testing on the 500-lb/h (227-kg/h) unit showed that that baghouse operating conditions can affect the mercury removal for given sorbent injection conditions. This directed development of a numerical model that incorporates parameters, such as the variation in filter cake thickness with time and cleaning frequency. In a collaborative effort with Dr. Radisav Vidic from the University of Pittsburgh and Dr. Joseph Flora from the University of South Carolina, such a numerical model has been developed with data from the sorbent injection tests on the 500-lb/h (227-kg/h) unit [13]. The model is a two-stage mathematical model for mercury removal using powdered activated carbon injection upstream of a fabric filter system. The first stage of the model accounts for removal in the ductwork, while the second stage accounts for additional removal due to the retention of carbon particles on the fabric filter. Mercury removal in the activated carbon particle is modeled using a pore diffusion model with the Langmuir isotherm describing equilibrium between the vapor-phase mercury and the mercury on the carbon particle surface. Mercury removal in the ductwork is modeled using a plug flow system while mercury removal in the fabric filter is modeled using a growing-bed, packed-bed approach. The presence of an external mass transfer boundary layer is accounted for in both stages. Advection, dispersion and a periodic cleaning interval are accounted for in the growing packed bed.

The model shows that removal in the ductwork is minimal for the conditions tested and that the additional carbon detention time from the entrapment of the carbon particles in the fabric filter enhances the mercury removal from the gas phase. The model predictions of the performance of the fabric filter were in good agreement with the experimental data. A sensitivity analysis with the model indicates that mercury removal is dependent on the isotherm parameters (which are in turn dependent on the flue gas temperature), the carbon-to-Hg ratio, the cleaning frequency and the fraction of the bed cleaned [13,14].

5. Conclusions

The laboratory-scale packed-bed reactor has proven to be useful in screening sorbents. Several attractive alternatives to activated carbon have been identified. These sorbents include metal oxides, metals sulfides and a sorbent produced from a novel process currently being developed. Sorbent capacities are higher for lower temperatures based on tests using the packed-bed reactor. Addition of sulfur promoter does not significantly improve the capacity of activated carbon for packed-bed reactors.

The pilot-scale combustion unit is well-suited for comparing novel sorbents with commercial activated carbon. A database has been developed which allows direct comparison of the performance of novel sorbents with removals achieved with Darco® FGD at similar operating conditions. Tests of a sorbent produced from a novel process showed promising results. Additional tests are planned with different coal types (for example, sub-bituminous coal).

The QGIS probe developed by Apogee Scientific has been presently found to be the only gas–solid separation technique capable of use in the measurement of in-duct vapor-phase mercury concentrations. The QGIS probe was used successfully in conjunction with a SCEM and a solid sorbent sampling method to measure in-duct removals in a slipstream, as well as in the full flow stream of the pilot combustion unit. Further testing in the pilot combustion unit will be conducted using a Powder River Basin sub-bituminous coal.

A mathematical model, jointly developed with researchers from two universities, will provide insight into the data obtained from the pilot-scale system. Sensitivity studies have quantified the parameters most likely to impact mercury removals. Enhancements are planned for the mathematical model focussing on in-duct removals. Data from the slipstream and full-flow stream of the pilot unit will be used in this enhancement effort.

Acknowledgements

The DOE/NETL Air Toxics Sampling Team conducted the flue gas measurements and preparation, recovery and analyses of sampling trains. This team consists of DOE personnel (Michael Hiltermann, Clement Lacher, Paul Rohar, Dennis Stanko and Arthur Wells, in addition to the authors) and Parsons Project Services personnel (Robert Thompson, Bill Garber and Chuck Perry). Parsons Project Services personnel (Jeffrey Palcic, William Brown, Dennis Nodd and the operations crew) were responsible for operation of the pilot combustion unit and ancillary systems. Parsons Project Services

personnel (Deborah Hreha) also provided additional laboratory support in preparation and analysis of solid samples.

References

- [1] E.J. Granite, H.W. Pennline, R.A. Hargis, Novel sorbents for mercury removal from flue gas, *Ind. Eng. Chem. Res.* 39 (2000) 1020–1029.
- [2] E.J. Granite, H.W. Pennline, Photochemical removal of mercury from flue gas, *Ind. Eng. Chem. Res.* 41 (2002) 5470–5476.
- [3] R.A. Hargis, W.J. O'Dowd, H.W. Pennline, Pilot-scale research at NETL on sorbent injection for mercury control, Presented at the 26th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, March.
- [4] R.A. Hargis, W.J. O'Dowd, H.W. Pennline, Mercury control by injection of activated carbon, Presented at the 17th Annual Pittsburgh Coal Conference, Pittsburgh, PA, September, 2000.
- [5] Method 101A, Code of Federal Regulations, 40CFR61, Appendix B, 1996.
- [6] ASTM D6784-02, Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario-Hydro Method), 2002.
- [7] E.M. Prestbo, et al., Solid Sorbent Method: Results of a Performance Based Measurement System (PBMS) Validation Study, Report to the EPA Air Pollution Prevention and Control Division, National Risk Management Research Laboratory, RTP, NC, 2001.
- [8] Energy and Environmental Research Center, Evaluation of Flue Gas Mercury Speciation Methods, EPRI TR-108988, Final Report, December, 1997.
- [9] W.J. O'Dowd, R.A. Hargis, H.W. Pennline, Pilot-scale research at NETL on mercury measurement and control, Presented at the 27th International Technical Conference on Coal Utilization and Fuel Systems, March, 2002.
- [10] H.W. Pennline, E.J. Granite, M.C. Freeman, R.A. Hargis, W.J. O'Dowd, A technique to control mercury from flue gas, 2002 AIChE Annual Meeting, Indianapolis, IN, November.
- [11] MSP Eliminating Particle-Related Artifacts in the Real-Time Measurement of Mercury in Flue Gases: Final Report Phase I, U.S. DOE SBIR Phase I Application No. 06013-99-1, April 28, 2000.
- [12] S. Sjostrom, T. Ley, R. Slye, Continuous real-time monitoring of mercury in flue gas from coal-fired boilers: field experience, Presented at the 27th International Technical Conference on Coal Utilization and Fuel Systems, March 2002.
- [13] J.R.V. Flora, et al., Modeling sorbent injection for mercury control in baghouse filters: I. Model development and sensitivity analysis, *J. Air Waste Manage. Assoc.* 53 (2003) 478–488.
- [14] J.R.V. Flora, et al., Modeling sorbent injection for mercury control in baghouse filters: II – Pilot –scale studies and model evaluation, *J. Air Waste Manage. Assoc.* 53 (2003) 489–496.